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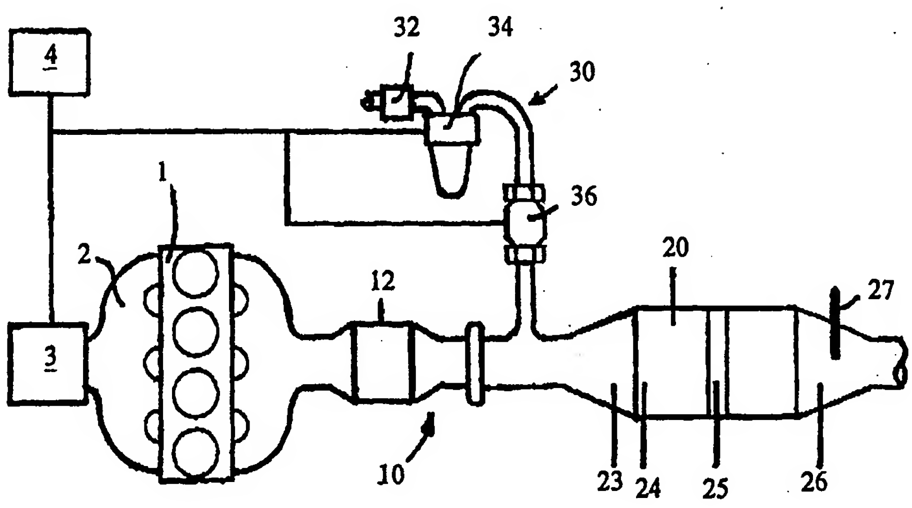
(54) Title: METHOD OF DE–SULPHURATING ENGINE EXHAUST NOx TRAPS



(57) Abstract

A method is disclosed for de–sulphurating a NOx trap in an engine and exhaust system which comprises heating the NOx trap (20) in a reducing atmosphere to a temperature at which sulphur is eliminated from the NOx trap by causing an exothermal reaction in the NOx trap between fuel–rich exhaust gases and additional oxygen introduced into the exhaust system upstream of the NOx trap.

Method of De-Sulphurating Engine Exhaust NOx Traps

This invention relates to methods of de-sulphurating engine exhaust NOx traps.

One known technique for improving the fuel economy of internal combustion engines is to design the engine to operate with leaner fuel mixtures, that is with mixtures of air and fuel having oxygen in excess of that which is required to produce complete combustion of the fuel. Such engines are known as "lean-burn" engines. As is well known to those skilled in the art, air-fuel mixture are characterised by a λ-value. For a given mass of air-fuel mixture, λ is the mass of air (or oxygen) in the mixture relative to the smallest mass of air (or oxygen) required to complete combustion of the fuel. Thus exactly stoichiometric mixtures of fuel and air have λ-values of 1.0; lean air-fuel mixtures have λ-values greater than 1.0, and rich air-fuel mixtures have λ-values less than 1.0.

In order to meet regulations regarding the emission of hydrocarbons, carbon monoxide and nitrogen oxides (NOx) from internal combustion engines, engine exhaust systems typically include a so-called three-way catalyst, which catalyses the combustion of those gases to water, carbon dioxide and nitrogen. Although conventional three-way catalysts perform satisfactorily on exhaust gases produced by stoichiometric or fuel-rich mixtures, they are much less effective in treating NOx where the exhaust gases are oxygen-rich, as when an engine is operated with lean fuel mixture. For this reason, it has been proposed (as for example described in US-A-5,388,403) to incorporate a device known as a NOx trap in exhaust systems for lean-burn engines downstream from three-way catalyst. The composition of NOx traps is know to those skilled in the art and typically comprises a mixture of salts of alkali metals (e.g. Li, K, Na, or Cs), alkaline earth metals (e.g. Ba or Cs),

lanthanides (e.g. LA or Y), transition metals (e.g. Fe or Cu) and noble metals (e.g. Pt) deposited on an inert substrate such as alumina.

NOx traps of this kind operate most effectively within a particular temperature range, and it is known to incorporate means for controlling the temperature of the NOx trap. In this respect, US-A-5,404,719 discloses a system for maintaining a NOx trap within its optimum temperature range in which additional fuel is introduced into the exhaust system upstream of the NOx trap to heat the NOx trap when the temperature drops below a desired minimum, and additional air is introduced into the exhaust system to cool the NOx trap when its temperature rises above a desired maximum. US-A-5,388,406 discloses a NOx trap incorporating an electrical element for heating the NOx trap to its operating temperature range.

Since NOx traps have a limited capacity for NOx, they must be regularly regenerated. This is achieved by periodically heating the NOx trap in a reducing atmosphere, e.g. by operating the engine with a stoichiometric or fuel-rich mixture. Under these conditions, NOx is desorbed from the NOx trap and released into the exhaust gases as nitrogen.

Sulphur oxides (SOx) are present in exhaust gases in smaller quantities than NOx, and are absorbed by the NOx trap at the same sites. However, SOx are not desorbed under the same conditions as NOx. Consequently, over time, the efficiency of the NOx trap decreases, and the NOx trap must be further treated to eliminate absorbed SOx. Elimination of SOx, i.e. de-sulphuration, can be achieved by heating the NOx trap in a reducing atmosphere to a temperature in excess of 550°C. US-A-5,402,641 discloses a process for de-sulphurating NOx traps in an engine and exhaust system in which the air-fuel ratio of the mixture fed to the engine is

automatically enriched with fuel when the temperature of the exhaust gases in the region of the NOx trap exceed 550°C, thereby inducing the elimination of SOx from the NOx trap. This system suffers from the disadvantage that the de-sulphuration process is triggered only when the NOx trap reaches a predetermined temperature. The de-sulphuration process cannot therefore be induced at pre-determined time intervals, as part of an overall engine emissions control strategy.

As claimed in the present invention, a method of de-sulphurating a NOx trap in an engine and exhaust system comprises heating the NOx trap in a reducing atmosphere to a temperature at which sulphur is eliminated from the NOx trap by causing an exothermal reaction between fuel-rich exhaust gases and oxygen introduced into the exhaust system upstream of the NOx trap.

The invention also provides an engine and exhaust system comprising an internal combustion engine having an intake through which a mixture of air and fuel can be introduced into the engine for combustion, engine control means for varying the air-fuel ratio of the mixture, an exhaust system connected to the engine for receiving exhaust gases from the engine, a NOx trap mounted in the exhaust system for removing nitrogen oxides from the exhaust gases, and a secondary air supply for introducing air into the exhaust gases upstream of the NOx trap, characterised in that the control means is arranged periodically to supply a fuel rich mixture to the engine and simultaneously to supply secondary air into the exhaust gases so as to cause an exotherm sufficient to drive sulphur-bearing contaminants from the NOx trap.

Elimination of SOx from NOx traps does not normally begin until about 550°C. The NOx trap is therefore preferably heated to at least 550°C, and preferably 600°C.

Over-heating of the NOx trap must also be avoided in order to preserve the life of the catalyst and its container. The NOx trap is therefore preferably heated to a temperature no higher than 800°C.

The reducing atmosphere may be created by adding fuel to the exhaust system. The source of fuel may be the engine fuel supply line or alternatively, where the vehicle includes a fuel vapour trap to absorb vapour from the fuel tank, the additional fuel may be provided by purging the vapour trap. Preferably however the additional fuel is create by running the engine on a fuel-rich mixture, preferably a mixture having a λ-value of from 0.7-0.9, e.g. about 0.8.

In order that the invention may be better understood, a preferred embodiment thereof will now be described, by way of example only with reference to the accompanying drawings, in which:

Figure 1 is a schematic drawing of an engine and exhaust system in accordance with the present invention; and

Figure 2 is a graph showing the variation in temperature of a NOx trap incorporated in the system of Figure 1 together with changes in the operating conditions of the engine

Figure 1 illustrates schematically an engine and exhaust system comprising a 1.8 litre 4-cylinder gasoline internal combustion engine 1 having an intake 2 into which a fuel injection system 3 introduces a mixture of air and fuel. The fuel injection system 3 is operated by an electronic engine control 4 that permits the air-to-fuel ratio of ratio of the mixture to be varied from fuel rich ($\lambda < 1.0$), through to stoichiometric ($\lambda = 1.0$) to lean ($\lambda > 1.0$). An exhaust system 10 is connected to the engine through which exhaust gases from the engine are discharged

to the atmosphere. The exhaust system 10 comprises a catalyst unit 12 mounted in close proximity to the engine 1 and containing a conventional three-way catalyst material capable of catalysing the combustion of hydrocarbons and carbon monoxide to water and carbon dioxide, and, when the engine is running under fuel-rich conditions, the reduction of nitrogen oxides (NOx). A NOx trap 20, also of conventional construction is mounted in the exhaust system downstream from the three-way catalyst unit 12 to absorb any NOx in the exhaust gases not treated by the catalyst unit 12. The NOx trap used in this example has a volume equal to 150% of the swept volume of the engine 1, but in practice NOx traps of smaller volumes, for example 100% or the swept volume of the engine, may be used. In order to demonstrate the effect of the invention, four temperature sensors 23, 24,25 and 26 are positioned in the NOx trap. The first sensor 23 is positioned immediately upstream of the NOx trap, the second sensor 24 is positioned 2.5cm downstream of the upstream end of the NOx trap, the third sensor 25 is positioned at the centre of the NOx trap sensor, and the fourth sensor 26 immediately downstream of the NOx trap. An exhaust gas oxygen sensor 27 is positioned immediately downstream of the NOx trap to monitor the oxygen content of the gases leaving the NOx trap.

A secondary air supply 30 is connected to the exhaust system 10 between the catalyst unit 12 and the NOx trap 20, and comprises an air filter 32, and air pump 34 and a control valve 36. The air pump 34 and the control valve 36 are operated by the engine control 4.

Under normal operating conditions the engine 1 runs with a lean air-fuel mixture. Hydrocarbons and carbon monoxide in the exhaust from the engine 1 are oxidised in the catalyst unit 12, but some NOx pass through the catalyst and are absorbed in the NOx trap 20. Traces of SOx passing through the catalyst unit 3 are also absorbed in the NOx

trap. The engine control 4 is arranged to purge the NOx trap regularly of NOx by running the engine 1 with a fuel-rich mixture. The engine control 4 is also conditioned to de-sulphurate the NOx trap 20 by running the engine with a fuel-rich mixture whilst air is introduced into the exhaust system 10 from the air pump 34 through the control valve 36. The amount of air added through the secondary air system is sufficient to produce an overall air-fuel mixture that is lean of stoichiometric, i.e. with a λ-value greater than i.0, preferably between 1.0 and 1.2, e.g. 1.1. Overall air-fuel mixtures that are fuel-rich should be avoided since these will result in increased emissions of carbon monoxide and hydrocarbons. When the NOx trap has reached its operating temperature, the mixture of exhaust gas and secondary air in the exhaust system upstream of the NOx trap creates an exotherm, raising the temperature of the NOx trap sufficiently to eliminate SOx therefrom.

During this, since the engine is being operated with a fuel-rich mixture, the three-way catalyst in the catalyst unit 12 is effective in catalysing the reduction NOx so that the non-functioning of the NOx trap does not adversely affect the NOx content of the gases emitted from the exhaust system. Moreover, the oxidising environment within the NOx trap itself ensures that any carbon monoxide and hydrocarbons in the exhaust gases are oxidised.

Figure 2 illustrates graphically the results of a test on the engine 1 when operated under these conditions. The test was conducted over a time interval, *t*, indicated in seconds on the abscissa of the graph. The engine was taken through a repeating cycle of accelerations and decelerations simulating driving a vehicle fitted with the engine under urban driving conditions. The solid line 41 shows the simulated variation in vehicle speed *V* in kilometres per hour as indicated on the right hand ordinate of the graph. Throughout this period, the engine was operated with a

stoichiometric air-fuel ratio, except for two periods *T1*, from 160 to 250 seconds from start up and *T2*, from 530 to730 seconds from start up, when the engine was operated with a fuel-rich mixture having a λ-value of 0.8.

The temperature of the exhaust gas immediately upstream of the NOx trap as detected by the first temperature sensor 23 rose steadily from ambient over the first 400 seconds of the test to a roughly constant level between 400 and 500°C, as indicated by the broken line 42.

Referring now to the black-dotted line 43 in Figure 2, the temperature of the NOx trap 2.5 cm from the upstream end, as detected by the second temperature sensor 24 also rose to a final temperature of about 500°C over this period, but increased to a peak of 750°C during the period T1 and to a peak of almost 1000°C during the period T2, confirming that the mixture of secondary air and fuel in the exhaust gas during these periods produced an exotherm in the NOx trap. These exotherms were detected in the centre of the NOx trap 20 and at the downstream end of the NOx trap by the temperature sensors 25 and 26, the outputs of which are shown respectively by the white-dotted line 43 and the chain-dotted line 44. Since the exotherm is generated over the upstream part of the trap and the heat generated is then carried downstream by convection, the peak exotherms are detected later in the centre and downstream ends of the NOx trap, and the maximum temperature reached is lower in the middle of the trap than at the upstream end, and lower again at the downstream end. The rate of propagation of the exotherm through the trap depends upon the rate of flow of exhaust gases and the heat capacity of the NOx trap. In order to ensure that the NOx trap is fully de-sulphurated, the whole of the trap should be heated to the de-sulphuration temperature. As indicated in Figure 2, where the engine is being used in a typical urban drive cycle, the whole body of the NOx trap can be heated to a temperature in

excess of 600°C, which is sufficient to purge the NOx trap of sulphur, within a period of from 90 to 200 seconds. Where a NOx trap of smaller volume is used, it would be possible to purge the trap in a smaller period. For example a NOx trap having a volume equal to that of the engine capacity (1.81) would probably be purged within 50 to 100 seconds.

In order to avoid over-heating of and consequent damage to the NOx trap during de-sulphuration, the temperature of the NOx trap should preferably be controlled so as not to exceed about 800°C, and should desirably be kept to an operating temperature of 650-750°C, e.g. about 700°C. This may be achieved by providing a direct input to the engine control unit 4 from a temperature sensor in the NOx trap. Alternatively temperature control can be programmed into the engine control unit 4 by using a software model to estimate the temperature of the NOx trap during operation of the engine and using this model to control the timing of the simultaneous enrichment of the fuel mixture and delivery of secondary air so that the temperature of the NOx trap is maintained at a target temperature.

In order to provide fully automatic de-sulphuration of the NOx trap, the engine control unit may include additional control software that models the rate of contamination of the NOx trap by sulphur and initiates a de-sulphuration cycle at appropriate intervals, each cycle being initiated only when the NOx trap has reached its normal operating temperature, which is 200°-300°C.

The invention therefore provides a system for de-sulphurating NOx traps that can be initiated at any desired period during operation of the engine by running the engine with a fuel rich mixture and simultaneously adding oxygen to the exhaust immediately upstream of the NOx trap.

CLAIMS

1. A method of de-sulphurating a NOx trap in an engine and exhaust system comprising heating the NOx trap in a reducing atmosphere to a temperature at which sulphur is eliminated from the NOx trap by causing an exothermal reaction between fuel-rich exhaust gases and additional oxygen introduced into the exhaust system upstream of the NOx trap.

2. A method as claimed in claim 1, wherein the NOx trap is heated to a temperature of from 600° to 800°C

3. A method as claimed in Claim 1 or Claim 2, wherein the fuel rich exhaust gases are produced by running the engine on a fuel-rich mixture of air and fuel.

4. A method as claimed in Claim 3, wherein the mixture has a λ value of 0.7-0.90.

5. An engine and exhaust system comprising an internal combustion engine (1) having an intake (2) through which a mixture of air and fuel can be introduced into the engine for combustion, engine control means (4) for varying the air-fuel ratio of the mixture, an exhaust system (10) connected to the engine (1) for receiving exhaust gases from the engine, a NOx trap (20) mounted in the exhaust system (10) for removing nitrogen oxides from the exhaust gases, and a secondary air supply (30) for introducing air into the exhaust gases upstream of the NOx trap (20), characterised in that the control means (4) is arranged periodically to supply a fuel rich mixture to the engine (1) and simultaneously to supply secondary air into the exhaust gases so as to cause an exotherm sufficient to drive sulphur-bearing contaminants from the NOx trap (20).

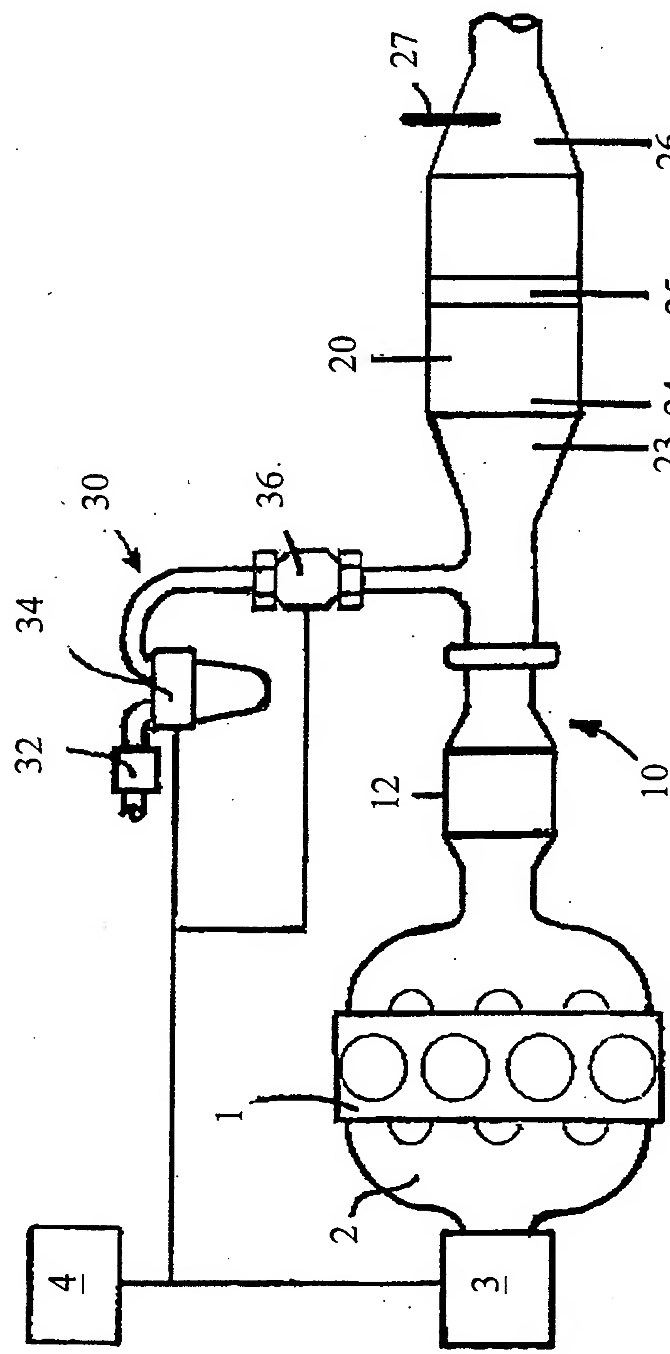


Figure 1

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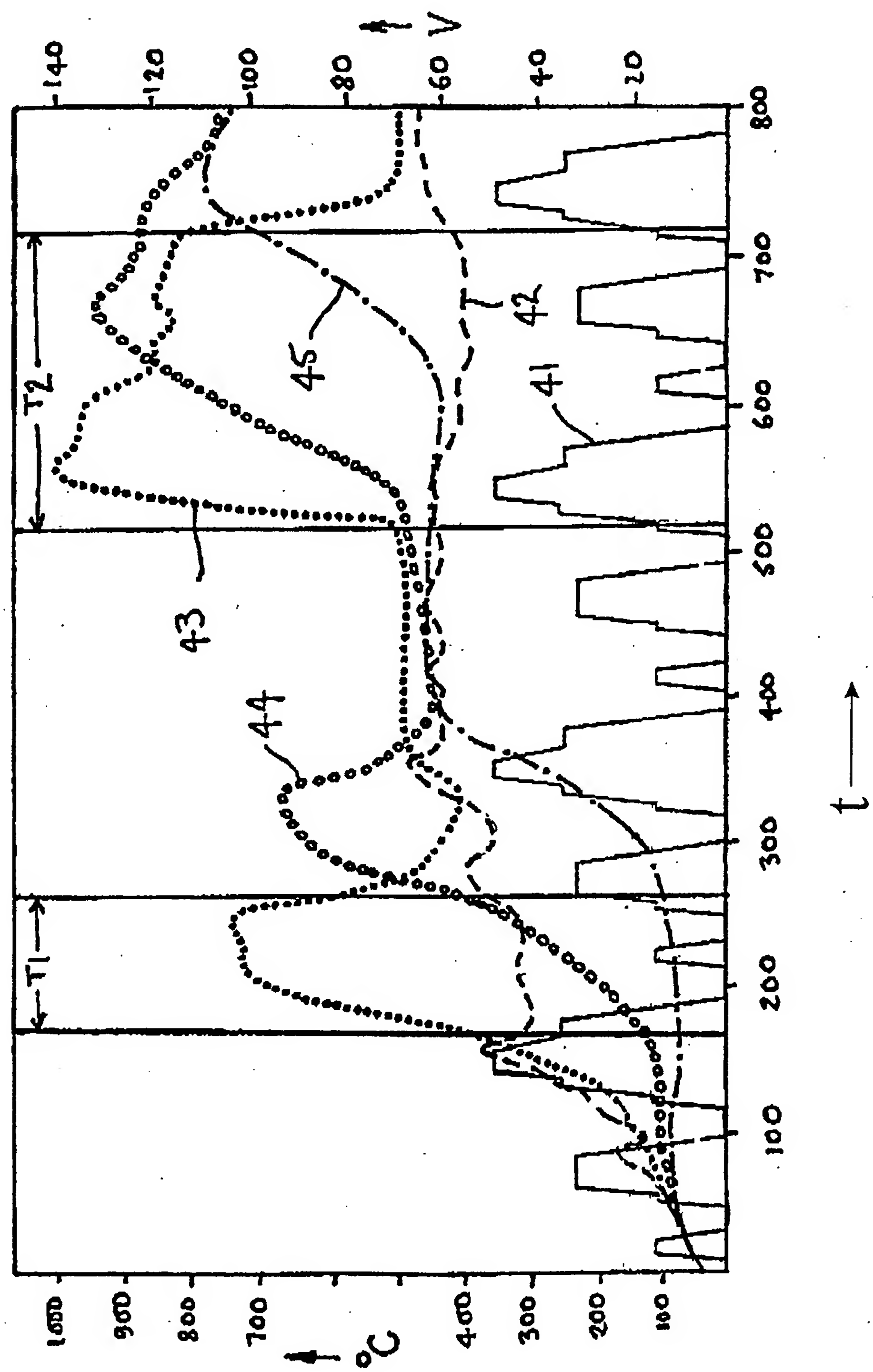
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Figure 2

INTERNATIONAL SEARCH REPORT

Int :ional Application No
PCT/GB 97/03369

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 F01N3/08 B01D53/94

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 580 389 A (TOYOTA MOTOR CO LTD) 26 January 1994 see column 4, line 17 - line 38 see column 5, line 26 - column 9, line 31; figures 1-8 ---	1-5
A	US 5 388 403 A (NAGAMI TETSUO ET AL) 14 February 1995 cited in the application see column 2, line 20 - column 3, line 16 see column 6, line 37 - column 9, line 34; figures 1,7,8 ---	1-5
A	EP 0 636 770 A (TOYOTA MOTOR CO LTD) 1 February 1995 see column 30, line 39 - column 31, line 41; figures --- -/--	1-5

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/GB 97/03369

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 095, no. 011, 26 December 1995 & JP 07 217474 A (TOYOTA MOTOR CORP), 15 August 1995, see abstract ---	1,5
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 310 (M-1620), 14 June 1994 & JP 06 066129 A (TOYOTA MOTOR CORP), 8 March 1994, see abstract ---	1,5
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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